Time Correlation Functions for Gases of Linear Molecules in a Magnetic Field

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(Z. Naturforsch. **27 a**, 721—732 [1972]; received 2 February 1972)

Time correlation functions for gases of linear molecules in a static homogeneous magnetic field are derived from the set of transport relaxation equations obtained from the linearized Waldmann-Snider equation. In particular, the complex auto- and cross correlation functions of the friction pressure tensor and the tensor polarization are considered. They are of importance for the viscosity, the depolarized Rayleigh spectrum, and flow birefringence. For the gases HD and CO_2 their real and imaginary parts are plotted as functions of a reduced time and discussed. Lastly, the influence of a constant magnetic field on the flow birefringence property of a gas of linear molecules in a Couette flow arrangement is treated. The principal axes of the dielectric tensor are rotated about the field direction. For two field orientations the respective angles of rotation are determined. The eigenvalues of the dielectric tensor reveal the tendency of the optical and transport properties of the gas to decouple for increasing field strengths.

Introduction

Transport-relaxation equations for the macroscopic variables characterizing the nonequilibrium state of a gas can be derived from a (generalized) Boltzmann equation by application of the moment method. For monatomic gases this has first been achieved by Maxwell[1]. Later, the method was extended by Grad[2]. For gases consisting of particles with internal degrees of freedom this solution procedure has been used extensively by Waldmann[3] and coworkers[4]. A large number of transport and relaxation phenomena have been treated by this approach. Particular mention should be made of the influence of external fields on transport properties (Senftleben-Beenakker effects[5]), magnetic relaxation[6], and light scattering[7].

Since the work of Kubo[8] and Mori[9] many researchers have directed their efforts toward a better understanding of a host of nonequilibrium phenomena in gases and liquids with the aid of time (and spatial) correlation functions. For a review see the articles of Zwanzig[10] and Steele[11]. The formal correlation function theory for the influence of external fields on the ordinary transport coefficients and on the Burnett coefficients of polyatomic gases has been developed by Gerhardts and Hajdu[12]. For the explicit calculation of transport coefficients from the exact correlation function expressions approximations have to be made. In conventional approaches approximations are introduced either by postulating some dynamical model which describes the microscopic happenings through equations of motion for the molecular variables (e. g. coordinates and momenta), or by resorting to some scheme in which macroscopic gradients are incorporated in an effective perturbation Hamiltonian.

It is the purpose of this paper to show that the transport-relaxation equations obtained from the Waldmann-Snider equation[13] can be used to calculate time correlation functions for gases of linear molecules. First, a general relation between the solution of the transport-relaxation equations and the time correlation functions is established. Then the auto-correlation functions for the friction pressure tensor, and the tensor polarization characterizing the alignment of the molecular rotational angular momentum, as well as their cross correlation function are calculated. The influence of a static homogeneous magnetic field is taken into consideration. These complex correlation functions are of importance for the viscosity coefficients[14], the spectrum of the depolarized Rayleigh scattering[7, 15], and the flow birefringence[7, 16] in molecular gases. Their real and imaginary parts are discussed and graphically displayed as functions of a reduced time for the gases HD and CO_2. Furthermore, the flow birefringence in a magnetic field is considered in detail, and for the experimental arrangement used by Baas[17] the angles are determined through which the principal axes of the dielectric tensor are rotated for two field orientations.

Recently, time correlation functions associated with the influence of a magnetic field on the heat conductivity and the viscosity of molecular gases

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have been calculated by KAPRAL and DESAI[18]. By a modification of the Chapman-Enskog solution procedure these authors developed a method for the calculation of time correlation functions from a generalized Boltzmann equation. For their explicit calculation they used the classical Kagan-Maksimov collision model[19] which, however (as they admit), is known from experiments[20] to give unrealistic results for the Senftleben-Beenakker effect on the viscosity. The experiments show that the tensor polarization (which cannot be treated by the Kagan-Maksimov model) is the dominant anisotropy term in the molecular distribution function which is responsible for the occurrence of the Senftleben-Beenakker effect on the viscosity of all gases except for NH_3 (cf. [21]).

I. Transport-Relaxation Equations and Time Correlation Functions

To establish a formal relation between the solution of the transport-relaxation equations and the time correlation functions, it is first outlined how these differential equations are derived from a kinetic equation for the one-particle distribution function $f = f(t, \boldsymbol{x}, \boldsymbol{p}, \boldsymbol{J})$. Here $\boldsymbol{x}$ and $\boldsymbol{p}$ are the space and linear momentum variables and $\hbar \boldsymbol{J}$ is the internal angular momentum operator. The local instantaneous average of an operator $\Psi(\boldsymbol{p}, \boldsymbol{J})$ is given by $n\langle\Psi\rangle = \mathrm{Tr}\int \mathrm{d}^3p\, \Psi f$ where $n = \mathrm{Tr}\int \mathrm{d}^3p\, f$ is the number density. The trace over the quantum numbers specifying the internal states of a molecule is denoted by "Tr". The distribution function f can be written as

$$f(t, \boldsymbol{x}, \boldsymbol{p}, \boldsymbol{J}) = f_0(p, J)\,(1 + \Phi(t, \boldsymbol{x}, \boldsymbol{p}, \boldsymbol{J})) \qquad (1)$$

where f_0 is the equilibrium distribution function (number density n_0) and Φ characterizes the deviation from the equilibrium state. For a dilute polyatomic gas the quantity Φ obeys the linearized Waldmann-Snider equation which can formally be written as

$$\partial\Phi/\partial t + \mathcal{L}\,\Phi = 0\,. \qquad (2)$$

Here the linear operator $\mathcal{L}$ is the sum of the flow term, the linearized collision term, and terms associated with the influence of external fields on the time evolution of the internal states of a molecule (see e. g. Refs. [4, 7]).

Now, the quantity Φ can be expanded with respect to a complete orthonormalized set of functions $\Phi_n = \Phi_n(\boldsymbol{p}, \boldsymbol{J})$ according to [22]

$$\Phi(t, \boldsymbol{x}, \boldsymbol{p}, \boldsymbol{J}) = \sum_n a_n(t, \boldsymbol{x})\; \Phi_n(\boldsymbol{p}, \boldsymbol{J})\,. \qquad (3)$$

Due to

$$\langle \Phi_n\, \Phi_{n'} \rangle_0 = \delta_{nn'}\,, \qquad (4)$$

where $\langle \ldots \rangle_0$ refers to an equilibrium average evaluated with f_0, the expansion coefficients (moments) a_n are given by

$$a_n = (n/n_0)\,\langle \Phi_n \rangle - \langle \Phi_n \rangle_0\,. \qquad (5)$$

The a_n are macroscopic variables characterizing the deviation of the gas from its equilibrium state. For small deviations the factor n/n_0 can be replaced by unity if $\Phi_n \neq 1$. Linear differential equations, called transport relaxation equations (TRE), for the time evolution of the a_n can be obtained by taking moments of Eq. (2) and using Eqs. (3), (4). With

$$\mathcal{L}_{nn'} = \langle \Phi_n\, \mathcal{L}\, \Phi_{n'} \rangle_0\,, \qquad (6)$$

the resulting TRE are

$$\frac{\partial a_n}{\partial t} + \sum_{n'} \mathcal{L}_{nn'}\, a_{n'} = 0\,. \qquad (7)$$

The formal solution of this system of differential equations can be written as

$$a_n(t) = \sum_{n'} C_{nn'}(t)\; a_{n'}(0)\;, \quad t > 0\,. \qquad (8)$$

Notice that $\mathcal{L}$ and consequently also $\mathcal{L}_{nn'}$ contain a gradient operator acting on $a_{n'}(t, \boldsymbol{x})$ which stems from the flow term. In Eqs. (7), (8) the space variable is dropped for simplicity. In general, the r.h.s. of Eq. (8) is of the form

$$\int C_{nn'}(t, \boldsymbol{x} - \boldsymbol{x}')\; a_{n'}(0, \boldsymbol{x}')\; \mathrm{d}^3x'.$$

If a spatial Fourier transformation is made, the gradient operator ∇ occurring in $\mathcal{L}$ and $\mathcal{L}_{nn'}$ is replaced by $i\,\boldsymbol{k}$ where $\boldsymbol{k}$ is the relevant wave vector. The spatial Fourier transform of the correlation function is needed in connection with the treatment of light scattering.

The functions $C_{nn'}(t)$ defined by Eq. (8) are time correlation functions. To see this, it is noticed that according to Eqs. (3), (4)

$$a_n(t) = \langle \Phi_n\, \Phi(t) \rangle_0\,. \qquad (9)$$

Now, the formal solution of Eq. (2) can be written as

$$\Phi(t) = \exp\{-\mathcal{L}\,t\}\; \Phi(0)\,. \qquad (10)$$

Substitution of Eq. (10) into Eq. (9) and use of the expansion, Eq. (3), for $\Phi(0)$ leads to

$$a_n(t) = \sum_{n'} \langle \Phi_n \exp\{-\mathcal{L}\, t\}\, \Phi_{n'} \rangle_0 \, a_{n'}(0) . \qquad (11)$$

Comparison of Eq. (11) with Eq. (8) yields the desired relation

$$C_{nn'}(t) = \langle \Phi_n \, \Phi_{n'}(t) \rangle_0 , \qquad (12)$$

where the $\Phi_{n'}(t)$ are defined by

$$\Phi_{n'}(t) = \exp\{-\mathcal{L}\, t\}\, \Phi_{n'} . \qquad (13)$$

Thus, alternatively to the conventional approaches mentioned above, an approximate expression for the time correlation function can be obtained from the solution of a truncated set of the infinite set of TRE. The results are equal if the same kinetic equation and the same (finite) subset of "basis functions" Φ_n is used in both cases.

II. Auto- and Cross-Correlation Functions for the Friction Pressure Tensor and the Tensor Polarization

a) Derivation

As an example of the use of transport relaxation equations for the calculation of time correlation functions the auto- and cross correlation functions of the friction pressure tensor and the tensor polarization are considered. The spatially homogeneous case (long wave length limit) is discussed. The relevant moments are the friction pressure tensor $\overline{\mathbf{p}} = \sqrt{2}\, p_0 \, \mathbf{a}_\eta$ ($p_0 = n_0 \, k_{\mathrm{B}} \, T_0$ is the equilibrium pressure; for the following treatment it is convenient to use the dimensionless quantity $\mathbf{a}_\eta$ instead of $\overline{\mathbf{p}}$), and the tensor polarization $\mathbf{a}_{\mathrm{T}} = C \langle (J^2 - \frac{3}{4})^{-1} \overline{\boldsymbol{J}\boldsymbol{J}} \rangle$ where C is an abbreviation for $\sqrt{\frac{15}{2}} \langle J^2/(J^2 - \frac{3}{4}) \rangle_0^{-1/2}$. Here the symbol "$\overline{\;\;}$" refers to the symmetric traceless part of a tensor. The application of the moment method to the linearized Waldmann-Snider equation yields the following pair of TRE (cf. Ref. [14]):

$$\partial \mathbf{a}_\eta / \partial t + \sqrt{2}\, \overline{\nabla \boldsymbol{v}} + \omega_\eta \, \mathbf{a}_\eta + \omega_{\eta \mathrm{T}} \, \mathbf{a}_{\mathrm{T}} = 0 , \qquad (14)$$

$$\partial \mathbf{a}_{\mathrm{T}} / \partial t + \omega_{\mathrm{H}} \, \mathsf{H} : \mathbf{a}_{\mathrm{T}} + \omega_{\mathrm{T}\eta} \, \mathbf{a}_\eta + \omega_{\mathrm{T}} \, \mathbf{a}_{\mathrm{T}} = 0 , \qquad (15)$$

where $\omega_{\mathrm{H}} = \gamma H$ and the quantities γ, H are respectively the gyromagnetic ratio and the magnetic field magnitude. The unit vector in the direction of the magnetic field is $\boldsymbol{h}$, and H is a fourth rank tensor which essentially describes the infinitesimal rotation of a 2-nd rank tensor [14] about $\boldsymbol{h}$. The relaxation coefficients ω_η, ω_{T} for the friction pressure tensor and the tensor polarization, and their cross coupling coefficients $\omega_{\eta\mathrm{T}}$, $\omega_{\mathrm{T}\eta}$ are collision integrals obtained from the linearized Waldmann-Snider collision term. Due to the time reversal invariance of the molecular interaction the Onsager symmetry $\omega_{\eta\mathrm{T}} = \omega_{\mathrm{T}\eta}$ holds. A moment's reflection shows that due to the term with $\overline{\nabla \boldsymbol{v}}$ the set of Eqs. (14), (15) is inhomogeneous which seems to be in contrast to Eq. (7). Notice, however, that the equation of motion (i. e. the moment equation for the velocity) together with Eqs. (14), (15) constitute a homogeneous set of equations [4]. For the remainder of this section the term $\overline{\nabla \boldsymbol{v}}$ is put equal to zero because the relevant correlation functions are obtained from the homogeneous set of equations. The presence of the magnetic field causes the rotational angular momentum to precess with frequency ω_{H} about $\boldsymbol{h}$.

For further treatment it proves convenient to introduce effectively spherical components of the tensors $\mathbf{a}_\eta$ and $\mathbf{a}_{\mathrm{T}}$ defined by

$$\mathbf{a}_\eta^{(m)} = \mathsf{P}^{(m)} : \mathbf{a}_\eta , \quad \mathbf{a}_{\mathrm{T}}^{(m)} = \mathsf{P}^{(m)} : \mathbf{a}_{\mathrm{T}} , \; m = 0, \pm 1, \pm 2 . \qquad (16)$$

The fourth rank projection tensors $\mathsf{P}^{(m)}$ derive from the Hamilton-Cayley equation for H, cf. Ref. [14]. Applying these projection tensors to Eqs. (14), (15), the TRE read:

$$\frac{\partial \mathbf{a}_\eta^{(m)}}{\partial t} + \omega_\eta \, \mathbf{a}_\eta^{(m)} + \omega_{\eta\mathrm{T}} \, \mathbf{a}_{\mathrm{T}}^{(m)} = 0 , \qquad (17)$$

$$\frac{\partial \mathbf{a}_{\mathrm{T}}^{(m)}}{\partial t} + (\omega_{\mathrm{T}} + \mathrm{i}\, m \, \omega_{\mathrm{H}}) \, \mathbf{a}_{\mathrm{T}}^{(m)} + \omega_{\eta\mathrm{T}} \, \mathbf{a}_\eta^{(m)} = 0 , \qquad (18)$$

where the property $\mathsf{P}^{(m)} : \mathsf{H} = \mathrm{i}\, m \, \mathsf{P}^{(m)}$ was used.

As outlined in the preceding section, the correlation functions of interest can be obtained from the solution of Eqs. (17), (18) according to

$$\mathbf{a}_\eta^{(m)}(t) = C_\eta^{(m)}(t) \, \mathbf{a}_\eta^{(m)}(0) + C_{\eta\mathrm{T}}^{(m)}(t) \, \mathbf{a}_{\mathrm{T}}^{(m)}(0) , \qquad (19)$$

$$\mathbf{a}_{\mathrm{T}}^{(m)}(t) = C_{\mathrm{T}\eta}^{(m)}(t) \, \mathbf{a}_\eta^{(m)}(0) + C_{\mathrm{T}}^{(m)}(t) \, \mathbf{a}_{\mathrm{T}}^{(m)}(0) . \qquad (20)$$

Here $C_{\eta}^{(m)}(t)$ and $C_{\mathrm{T}}^{(m)}(t)$ are the autocorrelation functions for the dimensionless friction pressure tensor and the tensor polarization; their cross correlation function is $C_{\eta\mathrm{T}}^{(m)}(t) = C_{\mathrm{T}\eta}^{(m)}(t)$. The time Fourier transform of $C_{\mathrm{T}}^{(m)}$ determines the spectrum associated with the depolarized Rayleigh scattering[7] in the high pressure case. The viscosity coefficients $\eta^{(m)}$ and the flow birefringence coefficients $\beta^{(m)}$, defined by

$$\overline{\mathbf{p}}^{(m)} = -2\,\eta^{(m)}\,\overline{\nabla\boldsymbol{v}}^{(m)}, \tag{21}$$

$$\overline{\boldsymbol{\epsilon}}^{(m)} = -2\,\beta^{(m)}\,\overline{\nabla\boldsymbol{v}}^{(m)}, \tag{22}$$

where $\overline{\mathbf{p}}$ is the friction pressure tensor and $\overline{\boldsymbol{\epsilon}}$ is the symmetric traceless part of the dielectric tensor, are related to the time integrals of $C_{\eta}^{(m)}$ and $C_{\eta\mathrm{T}}^{(m)}$ in the following way

$$\eta^{(m)} = p_0 \int_0^\infty \mathrm{d}t\, C_{\eta}^{(m)}(t), \tag{23}$$

$$\beta^{(m)} = -2\,\pi\, n_0 (\alpha_{\|} - \alpha_{\perp})\, \left(\langle J^2/(J^2 - \tfrac{3}{4})\rangle_0\right)^{1/2} \frac{1}{\sqrt{15}} \int_0^\infty \mathrm{d}t\, C_{\eta\mathrm{T}}^{(m)}(t). \tag{24}$$

Here $\alpha_{\|}$ and $\alpha_{\perp}$ are the molecular polarizabilities for an electric field parallel and perpendicular to the axis of a linear molecule. The physical meaning of the $\eta^{(m)}$ has been discussed by HESS and WALDMANN[14], the physical meaning of the $\beta^{(m)}$ and the derivation of Eqs. (23), (24) will be discussed in Section III and in the Appendix.

Explicit expressions for the time correlation functions can be readily obtained by Laplace transform techniques. We introduce the Laplace transformed quantities by

$$\tilde{\mathbf{a}}(s) = \int_0^\infty \mathrm{d}t\, e^{-st}\, \mathbf{a}(t). \tag{25}$$

Transforming Eqs. (17), (18) according to (25) we obtain a pair of coupled linear equations for $\tilde{\mathbf{a}}_{\eta}(s)$ and $\tilde{\mathbf{a}}_{\mathrm{T}}(s)$ which after straightforward algebra decouple into

$$\tilde{\mathbf{a}}_{\eta}^{(m)}(s) = \tilde{C}_{\eta}^{(m)}(s)\, \mathbf{a}_{\eta}^{(m)}(0) + \tilde{C}_{\eta\mathrm{T}}^{(m)}(s)\, \mathbf{a}_{\mathrm{T}}^{(m)}(0), \tag{26}$$

$$\tilde{\mathbf{a}}_{\mathrm{T}}^{(m)}(s) = \tilde{C}_{\mathrm{T}\eta}^{(m)}(s)\, \mathbf{a}_{\eta}^{(m)}(0) + \tilde{C}_{\mathrm{T}}^{(m)}(s)\, \mathbf{a}_{\mathrm{T}}^{(m)}(0). \tag{27}$$

In these equations we have

$$\tilde{C}_{\eta}^{(m)}(s) = (\Omega_m + s)\,(s - s_1)^{-1}\,(s - s_2)^{-1}, \tag{28}$$

$$\tilde{C}_{\eta\mathrm{T}}^{(m)}(s) = \tilde{C}_{\mathrm{T}\eta}^{(m)}(s) = -\,\omega_{\eta\mathrm{T}}(s - s_1)^{-1}(s - s_2)^{-1}, \tag{29}$$

$$\tilde{C}_{\mathrm{T}}^{(m)}(s) = (\omega_{\eta} + s)\,(s - s_1)^{-1}\,(s - s_2)^{-1}, \tag{30}$$

where

$$\Omega_m = \omega_{\mathrm{T}} + \mathrm{i}\, m\, \omega_{\mathrm{H}} \equiv \omega_{\mathrm{T}}(1 + \mathrm{i}\, m\, \varphi), \tag{31}$$

and φ is the angle through which the rotational angular momentum precesses in the time $1/\omega_{\mathrm{T}}$. The quantities s_1 and s_2 are the roots of the quadratic equation $(\Omega_m + s)\,(\omega_{\eta} + s) - \omega_{\eta\mathrm{T}}^2 = 0$. The desired time correlation functions are obtained by applying to Eqs. (26), (27) the inverse Laplace transform to Equation (25). Comparison with Eqs. (19), (20) then gives the result

$$C_{\eta}^{(m)}(t) = (s_1 - s_2)^{-1}[(\Omega_m + s_1)\, e^{s_1 t} - (\Omega_m + s_2)\, e^{s_2 t}], \tag{32}$$

$$C_{\mathrm{T}}^{(m)}(t) = (s_1 - s_2)^{-1}\,[(\omega_{\eta} + s_1)\, e^{s_1 t} - (\omega_{\eta} + s_2)\, e^{s_2 t}], \tag{33}$$

$$C_{\eta\mathrm{T}}^{(m)}(t) = C_{\mathrm{T}\eta}^{(m)}(t) = -\,\omega_{\eta\mathrm{T}}(s_1 - s_2)^{-1}\,[e^{s_1 t} - e^{s_2 t}]. \tag{34}$$

In Eqs. (32) – (34) the m-dependence of s_1, s_2 has not been explicitly denoted. According to Eq. (25) the time integral of a correlation function is simply given by

$$\int_0^\infty C_{\mathrm{AB}}(t)\,\mathrm{d}t = \tilde{C}_{\mathrm{AB}}(s = 0). \tag{35}$$

Equation (35) will be used in Section III.

b) Graphs and Discussion

For both the gases HD and CO$_2$ the coupling constant $R_{\eta\mathrm{T}} \equiv \omega_{\eta\mathrm{T}}/\omega_{\eta}$ is of the order 10^{-2} (cf. Ref. [7]). Consequently, it proves instructive to expand the correlation functions, Eqs. (32) – (34) in powers of this quantity. Retaining the lowest order only, we obtain

$$\operatorname{Re}\left(C_\eta^{(m)}(\tau)-C_\eta^{(0)}(\tau)\right)\approx R_{\eta\mathrm{T}}^2\,(R^2+R_m^2)^{-2}R^{-2}\,\{e^{-\tau}[R^2(R^2-R_m^2)\cos m\varphi\tau+2R^3R_m\sin m\varphi\tau-(R^2+R_m^2)^2]+R_m^2e^{-\tau'}[3R^2+R_m^2-R(R^2+R_m^2)\tau']\}\,, \tag{36}$$

$$\operatorname{Im}C_\eta^{(m)}(\tau)\approx R_{\eta\mathrm{T}}^2\,(R^2+R_m^2)^{-2}\{e^{-\tau}[2RR_m\cos m\varphi\tau-(R^2-R_m^2)\sin m\varphi\tau]-R_m e^{-\tau'}[(R^2+R_m^2)\tau'+2R]\}\,, \tag{37}$$

$$\operatorname{Re}C_\mathrm{T}^{(m)}(\tau)=e^{-\tau}\cos m\varphi\tau+O(R_{\eta\mathrm{T}}^2),\quad \operatorname{Im}C_\mathrm{T}^{(m)}(\tau)=e^{-\tau}\sin m\varphi\tau+O(R_{\eta\mathrm{T}}^2), \tag{38), (39}$$

$$\operatorname{Re}C_{\eta\mathrm{T}}^{(m)}(\tau)\approx R_{\eta\mathrm{T}}(R^2+R_m^2)^{-1}\{-e^{-\tau}[R\cos m\varphi\tau+R_m\sin m\varphi\tau]+Re^{-\tau'}\}\,, \tag{40}$$

$$\operatorname{Im}C_{\eta\mathrm{T}}^{(m)}(\tau)\approx R_{\eta\mathrm{T}}(R^2+R_m^2)^{-1}\{e^{-\tau}[R\sin m\varphi\tau-R_m\cos m\varphi\tau]+R_me^{-\tau'}\}\,, \tag{41}$$

where

$$R=1-\omega_\mathrm{T}/\omega_\eta=1-R_\mathrm{T};\;R_m=R_\mathrm{T}\,m\varphi;\;\tau=\omega_\mathrm{T}\,t;\;\tau'=\omega_\eta\,t\,. \tag{42}$$

Equation (36) is for $\operatorname{Re}[C_\eta^{(m)}(\tau)-C_\eta^{(0)}(\tau)]$, since $C_\eta^{(m)}(\tau)$ is m-independent in the zero-coupling limit $\omega_{\eta\mathrm{T}}\to 0$. Hence the magnetic field influence on the correlation function will be highlighted if we consider this difference instead of $\operatorname{Re}C_\eta^{(m)}(\tau)$ itself. The experimental values for R_T and $R_{\eta\mathrm{T}}$, which are taken from measurements of KORVING et al. [23] for room temperature (cf. Ref. [7], see also KEIJSER et al. [24]) are as follows: For HD, $R_\mathrm{T}=0.15$, $R_{\eta\mathrm{T}}=1.7\times10^{-2}$; for CO_2, $R_\mathrm{T}=1.3$, $R_{\eta\mathrm{T}}=7.9\times10^{-2}$. The values for ω_η, valid for a pressure of 1 atm, are: For HD, $\omega_\eta=10^{10}$ sec^{-1}; for CO_2, $\omega_\eta=7\times10^9$ sec^{-1}. Recent measurements on flow birefringence by BAAS [17] have shown that the sign of $\omega_{\eta\mathrm{T}}$ is positive for CO_2, and this should be true as well for HD as indicated by theoretical calculation [25]. Observe, that only $C_{\eta\mathrm{T}}^{(m)}$ is linear in $R_{\eta\mathrm{T}}$ in lowest order, whereas the other two correlation functions have no linear terms in $R_{\eta\mathrm{T}}$. Furthermore, all imaginary parts vanish for $m\varphi=0$. This is, of course, also true for the exact expressions, Equations (32) – (34).

In Figs. 1 – 10 are plotted the real and imaginary parts of the complex correlation functions for the gases HD and CO_2. The features of all the graphs $C_\eta^{(m)}-C_\eta^{(0)}$, $C_\mathrm{T}^{(m)}$, $C_{\eta\mathrm{T}}^{(m)}$ can satisfactorily be explained in light of the above expansions and the numerical values of R_T, $R_{\eta\mathrm{T}}$, and ω_η. The reduced time in these graphs is $\omega_\mathrm{T}\,t$, since $\exp\{-\omega_\mathrm{T}\,t\}$ multiplies the oscillatory terms. Thus, whereas $R_\mathrm{T}>1$ for CO_2, we have $R_\mathrm{T}\ll1$ for HD which implies that $\exp\{-\tau'\}$ ($\exp\{-\tau\}$) plays the less important role for HD (CO_2).

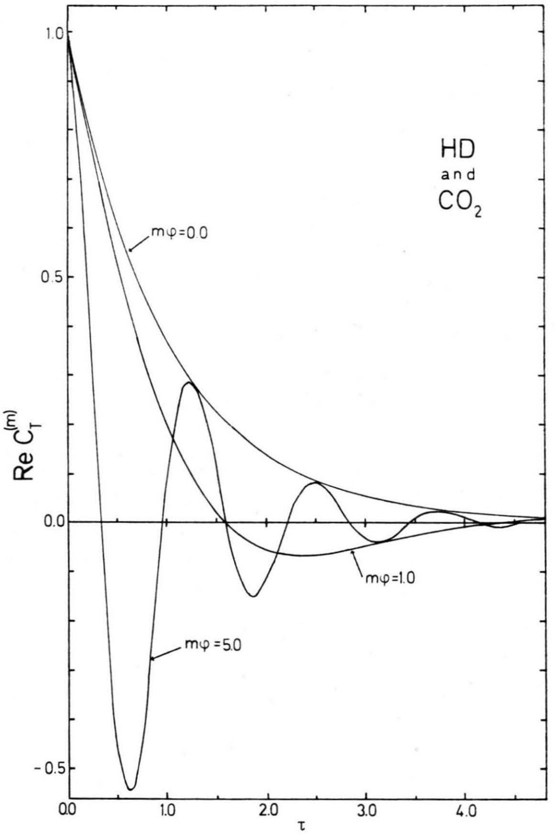

Fig. 1. $\operatorname{Re}C_\mathrm{T}^{(m)}(\tau)$ as a function of the reduced time $\tau=\omega_\mathrm{T}\,t$ for several values of $m\varphi$. See Eq. (38), which in lowest order is valid for both gases HD and CO_2.

The fact that Figs. 1 and 2 can apply for HD as well as for CO_2 is, of course, approximate and follows from our choice of reduced time scaling together with the smallness of $R_{\eta\mathrm{T}}^2$ ($\sim10^{-3}$). Correspondingly, in the lowest approximation, the $m\varphi=0$ curve appears to be the envelope for the $m\varphi=1.0$, 5.0 curves, in agreement with Equation (38). These correlation functions, which are proportional to

$$\langle\overline{\boldsymbol{J}\boldsymbol{J}}^{(m)}(t):\overline{\boldsymbol{J}\boldsymbol{J}}^{(-m)}(0)/[(J^2(t)-\tfrac34)(J^2(0)-\tfrac34)]\rangle_0$$

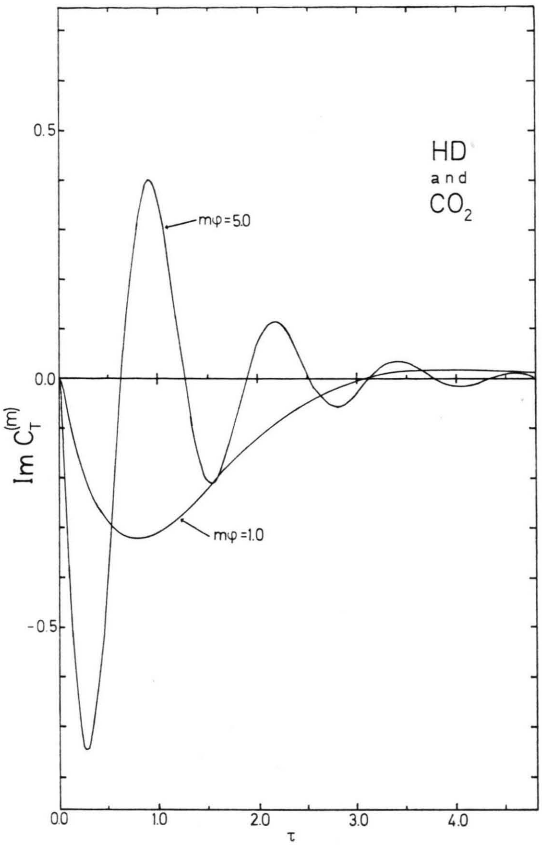

Fig. 2. Im $C_T^{(m)}(\tau)$ as a function of the reduced time τ for several values of $m\,\varphi$. See Equation (39).

influence the time behaviour of the other functions. Consequently, it is worthwhile to elaborate on the physical meaning of the precession of the tensor polarization in a magnetic field and the significance of $m=0$, ± 1, ± 2 in a schematic way as follows. The discussion will be restricted to the simplest case of a system with vanishing vector polarization but nonzero tensor polarization, viz. two particles in the rotational state $j=1$, with corresponding rotational angular momenta being in opposite directions. We can relate [26] the tensor polarization to the relative occupation numbers of the three magnetic substates, N_k $(k=+1, 0, -1)$, viz. $\langle\overline{J_z J_z}\rangle \propto (N_{+1}+N_{-1}-2\,N_0)$, where z is the direction of the axis of quantization. In our case we have $N_{+1}=N_{-1}=1/2$, $N_0=0$. In the course of the precession of the $\boldsymbol{J}$'s about the field direction $\boldsymbol{h}$, a configuration will repeat itself after turning through an angle φ_{R} such that $m\,\varphi_{\mathrm{R}}=2\,\pi$. Pictures for $m=0, 1, 2$ are shown in Figure 2 a. Notice that $m=0$, ± 1, ± 2 corresponds to the cases where $\boldsymbol{h}$ is parallel to the z axis, and makes an angle of 45° and 90°, respectively. The macroscopic tensor polarization occurring in a gas behaves in the same manner as far as the precession in the magnetic field is concerned. In the approach to equilibrium the magnetic substates will tend to become equally populated, i. e. $N_{+1}=N_{-1}=N_0=1/3$ for $j=1$. The loss of correlation of $\overline{\boldsymbol{J}\boldsymbol{J}}$ with its values at earlier times, induced via collisions, is governed in lowest approximation solely by the collision integral ω_{T}. The appearance of $R_{\eta\mathrm{T}}$ in higher orders represents an additional coupling of the tensor polarization to the macroscopic velocity field. The mechanism of this coupling is the same as for the decay of the tensor polarization, viz. collisions induced by a non-spherical potential [26].

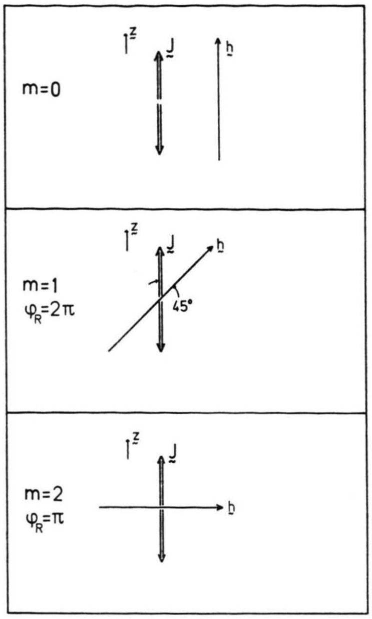

Fig. 2 a. The axis of quantization is $\boldsymbol{z}$. The direction of the magnetic field, about which $\boldsymbol{J}$ is precessing, is along $\boldsymbol{h}$. The angle for which the configuration in the course of precessing first repeats itself is φ_{R}. For all three cases shown, N_0 is assumed to be zero.

In Figs. 3, 4, and in Figs. 5, 6 are depicted the temporal behaviors of the real and imaginary parts, respectively, of the friction pressure tensor correlation function. The rate of decay of Re $C_\eta^{(m)}$ is, in 0-th order, solely given by the collision integral ω_η. According to Eq. (23), the areas enclosed by the various respective curves are proportional to the coefficients $\mathrm{Re}(\eta^{(m)}-\eta^{(0)})$ and $\mathrm{Im}\,\eta^{(m)}$. Recalling [14] that the dispersion-like curve, $\mathrm{Re}\,\eta^{(m)}$ versus φ, approaches a saturation value for large φ (or $m\,\varphi$), one sees that this is consistent with Figs. 3, 4, where-

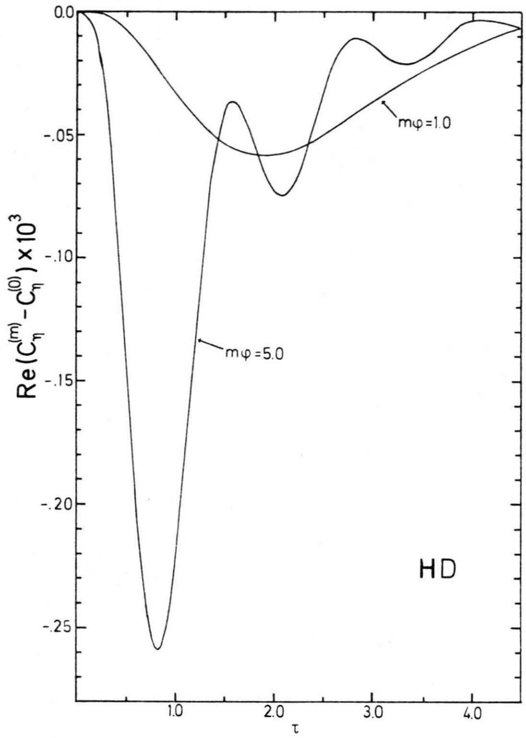

Fig. 3. Re $[C_\eta^{(m)}(\tau) - C_\eta^{(0)}(\tau)] \cdot 10^3$ as a function of the reduced time τ for several values of $m\varphi$ for the gas HD. See Equation (36).

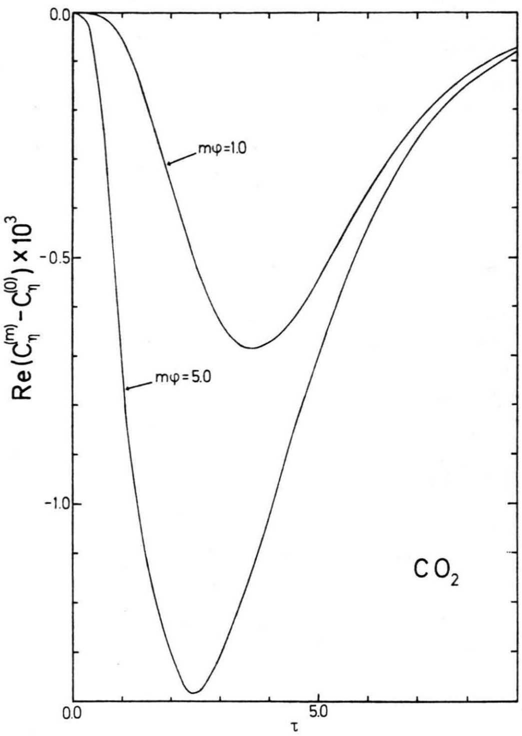

Fig. 4. Same as Fig. 3, except that the gas is CO_2.

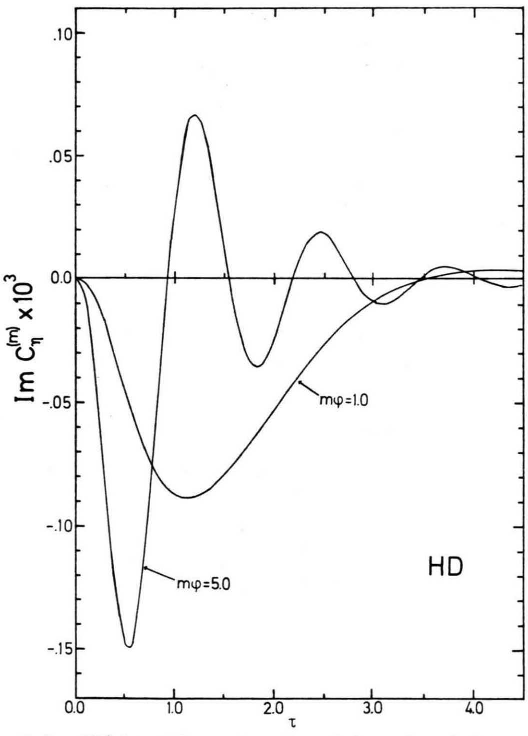

Fig. 5. Im $C_\eta^{(m)}(\tau) \cdot 10^3$ as a function of the reduced time τ for several values of $m\varphi$ for the gas HD. See Equation (37).

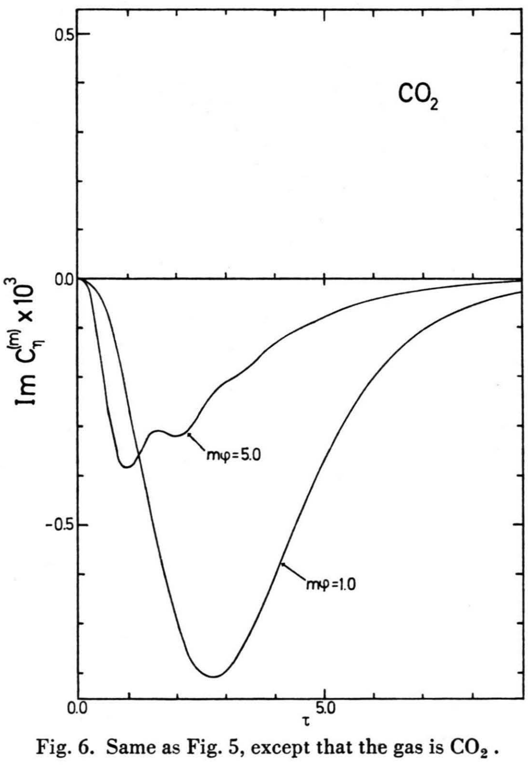

Fig. 6. Same as Fig. 5, except that the gas is CO_2.

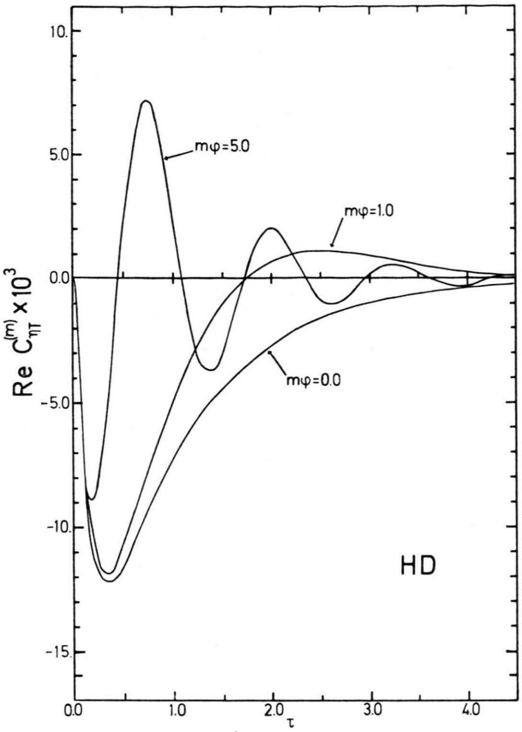

Fig. 7. Re $C_{\eta T}^{(m)}(\tau) \cdot 10^3$ as a function of the reduced time τ for several values of $m\ \varphi$ for the gas HD. See Equation (40).

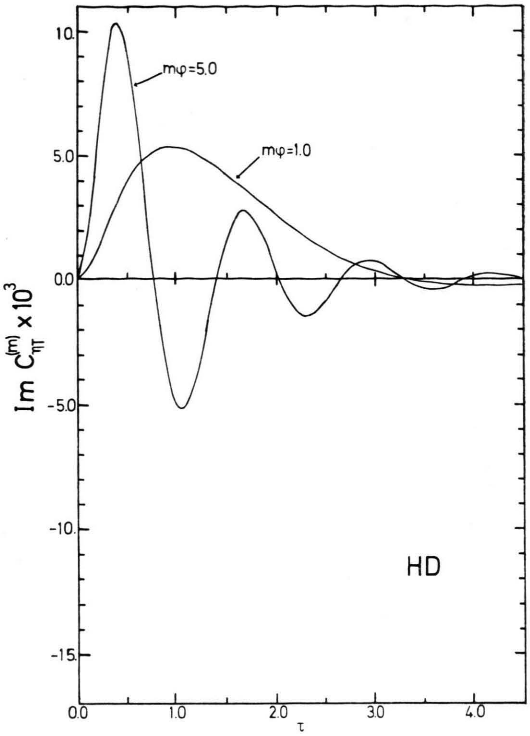

Fig. 9. Im $C_{\eta T}^{(m)}(\tau) \cdot 10^3$ as a function of the reduced time τ for several values of $m\ \varphi$ for the gas HD. See Equation (41).

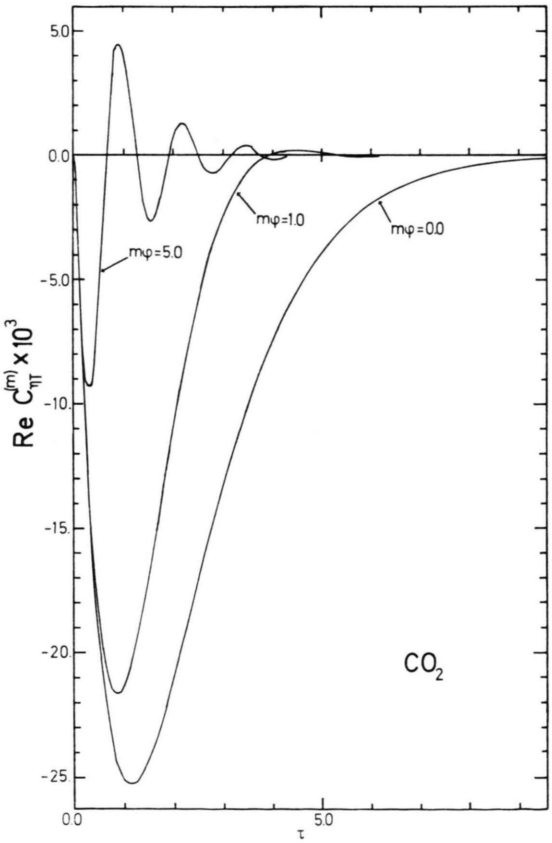

Fig. 8. Same as Fig. 7, except that the gas is CO_2.

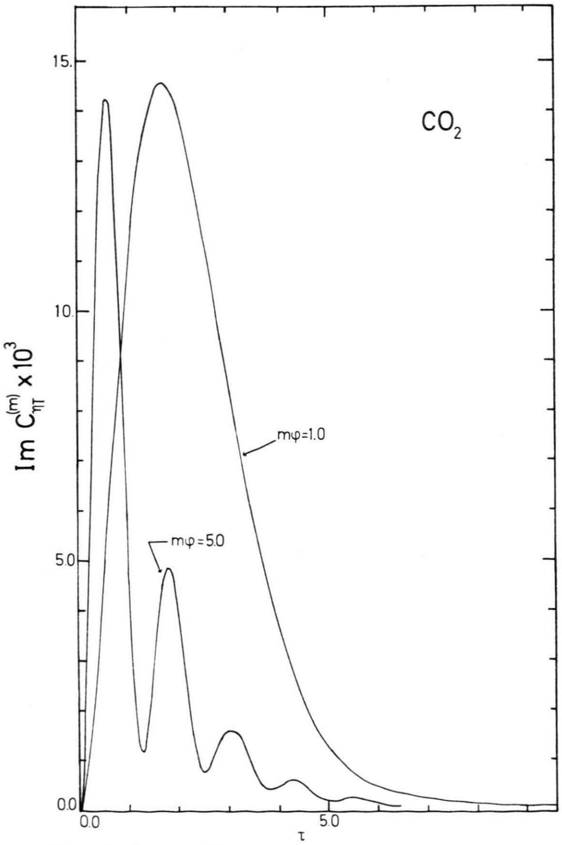

Fig. 10. Same as Fig. 9, except that the gas is CO_2.

in there is a larger area enclosed between the larger $m\,\varphi$-valued curve and the τ-axis. Indeed, the relative increase in area per increase in $m\,\varphi$-value is greater for CO_2, indicating the larger contribution of the non-spherical part of the intermolecular potential for these molecules than for HD molecules. On the other hand, the smaller areas enclosed by the $m\,\varphi = 5.0$ curves in Figs. 5, 6 (contrasted with $m\,\varphi = 1.0$) reflects the fact that the dispersion-like curve $\operatorname{Im} \eta^{(m)}(\varphi)$, approaches zero asymptotically as φ becomes arbitrarily large.

Figures 7 and 8 and Figs. 9 and 10 depict the real and imaginary parts, respectively of the cross correlation function which is proportional to

$$\langle \overline{\boldsymbol{v}\,\boldsymbol{v}}(t)^{(m)} : \overline{\boldsymbol{J}\,\boldsymbol{J}}^{(-m)}(0) / (J^2(0) - \tfrac{3}{4}) \rangle_0 \,.$$

In all cases the areas enclosed by the curves decrease for increasing values of $m\,\varphi$. Recalling Eqs. (22) and (24) this reveals the tendency for the optical and transport properties of the fluid to decouple and become independent of one another as the magnetic field strength increases, i. e. as many precessions take place between an effective collision time $1/\omega_{\mathrm{T}}$. And indeed, this tendency is more pronounced for CO_2, indicating the importance of the role played by the non-spherical part of the potential.

III. Flow Birefringence in a Magnetic Field

The phenomenon whereby a gas becomes birefringent due to the presence of a flow velocity field (or a sound field) has been discussed by HESS [7] and experimentally observed by BAAS [17]. We extend the treatment here to the case where a constant magnetic field is present. The point of departure is the constitutive relation, Eq. (22), which can be written here as

$$\overline{\boldsymbol{\epsilon}} = -2\,\boldsymbol{\beta} : \overline{\nabla \boldsymbol{v}} = -2 \sum_{m=-2}^{+2} \beta^{(m)}\, \mathbf{P}^{(m)} : \overline{\nabla \boldsymbol{v}}\,, \qquad (43)$$

where $\boldsymbol{\beta}$ now is the fourth rank "flow birefringence tensor" and $\beta^{(m)}$ is given by Equation (24). Evaluating the integral in Eq. (24) according to the prescription of Eq. (35), we obtain

$$\int_0^\infty \mathrm{d}t\, C_{\eta\mathrm{T}}^{(m)}(t) = -(\omega_{\eta\mathrm{T}}/\omega_\eta\, \omega_{\mathrm{T}})\, [1 - A_{\eta\mathrm{T}} + i\, m\, \varphi]^{-1}, \qquad (44)$$

where $A_{\eta\mathrm{T}} = R_{\eta\mathrm{T}}^2 / R_{\mathrm{T}}$. Consequently, we have

$$\beta^{(m)} = \beta / \big(1 + i\, m\, \varphi / (1 - A_{\eta\mathrm{T}})\big)\,. \qquad (45)$$

Introducing

$$\delta_m(\varphi) = \arctan(m\,\varphi)\,, \qquad (46)$$

we can rewrite Eq. (45) as

$$\beta^{(m)} \approx (\beta / \sqrt{1 + m^2 \varphi^2})\, \exp\{-i\, \delta_m(\varphi)\}\,. \qquad (47)$$

Since the ratio $A_{\eta\mathrm{T}}$ is of the order of 10^{-3}, its appearance in the radical and in the exponent of these last equations has been neglected to a very good approximation. The quantity β is the scalar "flow birefringence coefficient" [7]

$$\beta = 2\,\pi\, n_0 (\alpha_{\parallel} - \alpha_{\perp}) \frac{1}{\sqrt{15}} \langle J^2 / (J^2 - \tfrac{3}{4}) \rangle_0^{1/2} \frac{\omega_{\eta\mathrm{T}}}{\omega_{\mathrm{T}}} \frac{\eta}{p_0}\,. \qquad (48)$$

where the zero field viscosity is

$$\eta = \eta_{\mathrm{iso}} / (1 - A_{\eta\mathrm{T}})\,, \quad \eta_{\mathrm{iso}} = p_0 / \omega_\eta\,. \qquad (49)$$

In the absence of magnetic fields $\boldsymbol{\beta}$ becomes a product of the scalar β and the unit fourth rank tensor.

In order to obtain explicit expressions for the index of refraction differences we make recourse to a cylindrical Couette flow, as employed in the experiment of BAAS [17]. The unit vectors for defining a convenient local coordinate system in the streaming gas are $\boldsymbol{e}_\varrho$, $\boldsymbol{e}_\varphi$, and $\boldsymbol{e}_z = \boldsymbol{e}_\varrho \times \boldsymbol{e}_\varphi$, wherein $\boldsymbol{e}_\varrho$ points radially outward from the cylindrical axis, $\boldsymbol{e}_\varphi$ points in the azimuthal direction, and $\boldsymbol{e}_z$ has the direction along the axis. (The z-axis of this local coordinate system is determined by the direction of propagation of a narrowly confined laser beam.) If we assume that the spatial dependence of the velocity field is given entirely through $\boldsymbol{r} \cdot \boldsymbol{e}_\varrho$, it follows [7] that

$$\overline{\nabla \boldsymbol{v}} = G\, \overline{\boldsymbol{e}_\varrho\, \boldsymbol{e}_\varphi}\,. \qquad (50)$$

This also serves to define the magnitude G of the velocity gradient. For the zero field situation discussed by HESS [7] the principal axes of the dielectric tensor have the directions

$$\boldsymbol{e}_0 = \boldsymbol{e}_z\,, \quad \boldsymbol{e}_\pm = \frac{1}{\sqrt{2}} (\boldsymbol{e}_\varrho \pm \boldsymbol{e}_\varphi)\,. \qquad (51)$$

In addition to altering the magnitude of the $\beta^{(m)}$ coefficients, see Eq. (47), the presence of a constant magnetic field will result in a rotation of the dielectric tensor's principal axes. With regard to the orienting of the field direction, $\boldsymbol{h}$, two special arrangements lend themselves particularly well to analysis: Case (a), in which $\boldsymbol{h}$ is parallel to the cylinder axis, $\boldsymbol{e}_z$; and case (b), in which $\boldsymbol{h}$ is parallel to a radial vector $\boldsymbol{e}_\varrho$. The main result for both cases is that the principal axes, Eq. (51), are rotated about the respective $\boldsymbol{h}$-directions.

Evaluating Eq. (43) with the aid of explicit expressions for the projection tensors, $\mathbf{P}^{(m)}$, as given by HESS and WALDMANN [14], we obtain for case (a)

$$\overline{\boldsymbol{\epsilon}} = -4\,G\,\mathrm{Re}\,\{\beta^{(2)}\,\mathbf{P}^{(2)} : \overline{\boldsymbol{e}_\varrho\,\boldsymbol{e}_\varphi}\} \tag{52}$$

$$= \frac{2\,G\,\beta}{\sqrt{1+4\,\varphi^2}}\,\{\cos\delta_2\,\overline{\boldsymbol{e}_\varrho\,\boldsymbol{e}_\varphi} + \tfrac{1}{2}\sin\delta_2\,(\overline{\boldsymbol{e}_\varrho\,\boldsymbol{e}_\varrho} - \overline{\boldsymbol{e}_\varphi\,\boldsymbol{e}_\varphi})\}\,,$$

and for case (b)

$$\overline{\boldsymbol{\epsilon}} = -4\,G\,\mathrm{Re}\,\{\beta^{(1)}\,\mathbf{P}^{(1)} : \overline{\boldsymbol{e}_\varrho\,\boldsymbol{e}_\varphi}\} \tag{53}$$

$$= \frac{2\,G\,\beta}{\sqrt{1+\varphi^2}}\,\{\cos\delta_1\,\overline{\boldsymbol{e}_\varrho\,\boldsymbol{e}_\varphi} - \sin\delta_1\,\overline{\boldsymbol{e}_\varrho\,\boldsymbol{e}_z}\}\,.$$

Hence, the magnetic field arrangements, cases (a), (b), provide in principle a means of determining the $\beta^{(2)}$, $\beta^{(1)}$ components, respectively of the flow birefringence tensor $\boldsymbol{\beta}$. The value of $\beta^{(0)}$ is unaffected by the field's presence, as seen from inspection of Equation (45). For case (a), when $\boldsymbol{h} \parallel \boldsymbol{e}_z$, the rotated principal axes of $\overline{\boldsymbol{\epsilon}}$ (i. e. the eigenvectors) are

$$\boldsymbol{e}_0' = \boldsymbol{e}_z\,, \tag{54 a}$$

$$\boldsymbol{e}_+' = \cos\vartheta\,\boldsymbol{e}_\varrho + \sin\vartheta\,\boldsymbol{e}_\varphi = \cos\frac{\delta_2}{2}\,\boldsymbol{e}_+ + \sin\frac{\delta_2}{2}\,\boldsymbol{e}_-\,, \tag{54 b}$$

$$\boldsymbol{e}_-' = \sin\vartheta\,\boldsymbol{e}_\varrho - \cos\vartheta\,\boldsymbol{e}_\varphi = -\sin\frac{\delta_2}{2}\,\boldsymbol{e}_+ + \cos\frac{\delta_2}{2}\,\boldsymbol{e}_-\,, \tag{54 c}$$

where $\vartheta = \pi/4 - \delta_2/2$; the corresponding eigenvalues are

$$\varepsilon_0 = 0\,, \qquad \varepsilon_\pm = \pm\,G\,\beta/\sqrt{1+4\,\varphi^2}\,. \tag{55}$$

For case (b), when $\boldsymbol{h} \parallel \boldsymbol{e}_\varrho$, the rotated principal axes of $\overline{\boldsymbol{\epsilon}}$ are

$$\boldsymbol{e}_0' = \sin\delta_1\,\boldsymbol{e}_\varphi + \cos\delta_1\,\boldsymbol{e}_z\,, \tag{56 a}$$

$$\boldsymbol{e}_\pm' = \frac{1}{\sqrt{2}}\,(\boldsymbol{e}_\varrho \pm \cos\delta_1\,\boldsymbol{e}_\varphi \mp \sin\delta_1\,\boldsymbol{e}_z)\,, \tag{56 b}$$

and the corresponding eigenvalues are

$$\varepsilon_0 = 0\,, \qquad \varepsilon_\pm = \pm\,G\,\beta/\sqrt{1+\varphi^2}. \tag{57}$$

In both situations the principal axes $\boldsymbol{e}_0'$, $\boldsymbol{e}_\pm'$ reduce to Eq. (51) when the magnetic field becomes zero. The rotations are shown in Figure 11.

We designate as $n_\pm'$ the indices of refraction for light polarized in the directions $\boldsymbol{e}_\pm'$. Recalling that, when the light is polarized in the direction of the principal axis $\boldsymbol{e}_\pm'$, $n_\pm' = (\boldsymbol{e}_\pm' \cdot \boldsymbol{\epsilon} \cdot \boldsymbol{e}_\pm')^{1/2}$, where $\boldsymbol{\epsilon} \approx \mathbf{1} + \overline{\boldsymbol{\epsilon}}$ (for a dilute gas the isotropic part of the dielectric tensor can be replaced by unity), and utilizing the fact that $|\varepsilon_\pm| \ll 1$, we obtain in lowest order the index of refraction difference as

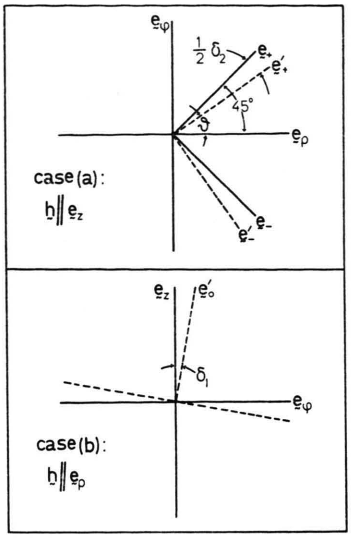

Fig. 11. In case (a) the magnetic field and the z-axis are directed out of the plane of the paper. For $\boldsymbol{e}_+'$ and $\boldsymbol{e}_-'$ see Equations (54 b, c). In case (b) the magnetic field and the $\boldsymbol{e}_\varrho$ axis are directed out of the plane of the paper. See Eqs. (56 a, b) for $\boldsymbol{e}_0'$, $\boldsymbol{e}_\pm'$. The unlabelled dotted line in case (b) is the intersection of the plane containing the principal axes $\boldsymbol{e}_\pm'$ with the plane of the drawing. The definition of the angles δ for cases (a) and (b) is given by Equation (46).

$$n_+' - n_-' = \sqrt{1+\varepsilon_+} - \sqrt{1-\varepsilon_+} \approx \varepsilon_+\,. \tag{58}$$

In order to realize case (a), wherein $\boldsymbol{h} \parallel \boldsymbol{e}_z$, the modification needed in Baas' experimental arrangement presents no unusual difficulties, since the direction of light propagation continues to remain along $\boldsymbol{e}_z$. For light polarized along the new principal axes, the index of refraction difference in lowest order, Eq. (58) becomes

$$n_+' - n_-' = G\,\beta/\sqrt{1+4\,\varphi^2}, \text{ when } \boldsymbol{h} \parallel \boldsymbol{e}_z\,. \tag{59}$$

The rotation of the axes as shown in Fig. 11 is also experimentally detectable. Furthermore, since the angle of rotation, δ_2, is an odd function of the precession angle [recall Eq. (46)], the sign of the gyromagnetic ratio for the molecule can be determined.

On the other hand for case (b), to set the direction of propagation along $\boldsymbol{h}$ is neither practicable nor desirable in the arrangement of Baas, since a straightforward detection of the rotation of the principal axes, as shown in Fig. 11, would not be achieved. However, retaining $\boldsymbol{e}_z$ as the direction of propagation, and selecting $\boldsymbol{e}_{\pm}$, as given by Eq. (51), to be the polarization directions, we obtain

$$n_+ - n_- \approx G\,\beta\cos\delta_1/\sqrt{1+\varphi^2} = G\,\operatorname{Re}\beta^{(1)} \qquad (60)$$

for the index of refraction difference. In deriving Eq. (60) the formula [27]

$$n^2 = D^2/\boldsymbol{D}\cdot\boldsymbol{E} = (\boldsymbol{\epsilon}\cdot\boldsymbol{E})\cdot(\boldsymbol{\epsilon}\cdot\boldsymbol{E})/\boldsymbol{E}\cdot\boldsymbol{\epsilon}\cdot\boldsymbol{E}\,, \qquad (61)$$

where $\boldsymbol{D} = \boldsymbol{\epsilon}\cdot\boldsymbol{E}$ is the displacement vector and $\boldsymbol{E}$ is the electrical field vector, was employed. Quadratic terms $G^2\,\beta^2$ were discarded, and the approximation $n_+^2 - n_-^2 = (n_+ + n_-)\,(n_+ - n_-) \approx 2\,(n_+ - n_-)$ was made. It follows then from Eqs. (46) and (47) that $\operatorname{Im}\beta^{(1)}$ can be calculated.

The precession angle φ is proportional to H/p_0, where H is the magnitude of the magnetic field and p_0 is the equilibrium pressure. Thus, if the velocity gradient G is known, a measurement of the index of refraction difference for selected values and orientations of the $\boldsymbol{H}$-field permits an independent determination of all components $\beta^{(m)}$ of the flow birefringence tensor.

In conclusion, it is recalled that the measurement of the flow birefringence for the field free case allows an experimental determination of $\omega_{\eta\mathrm{T}}/\omega_{\mathrm{T}}$. In the presence of a magnetic field the relaxation frequency ω_{T} can be determined independently if the gyromagnetic ratio is known. The advantage of such a determination of ω_{T} is that no other types of molecular alignment contribute to the effect. This is in contrast to the Senftleben-Beenakker effect of the viscosity.

Appendix

Connection between Transport Coefficients and Time Correlation Functions

It is briefly outlined, how the relations between transport coefficients and correlation functions, Eqs. (21), (22), can also be derived from the moment equations (14), (15). Having solved the homogeneous Eqs. (17), (18), we obtain readily the solution of the inhomogeneous equations (14), (15) as follows:

$$\begin{aligned}\mathbf{a}_\eta^{(m)}(t) &= C_\eta^{(m)}(t)\,\mathbf{a}_\eta^{(m)}(0) + C_{\eta\mathrm{T}}^{(m)}(t)\,\mathbf{a}_\mathrm{T}^{(m)}(0)\\ &\quad - \sqrt{2}\int_0^t C_\eta^{(m)}(t-t')\,\overline{\nabla\boldsymbol{v}}^{(m)}(t')\,\mathrm{d}t', \end{aligned} \qquad (\mathrm{A\,1})$$

$$\begin{aligned}\mathbf{a}_\mathrm{T}^{(m)}(t) &= C_{\eta\mathrm{T}}^{(m)}(t)\,\mathbf{a}_\eta^{(m)}(0) + C_\mathrm{T}^{(m)}(t)\,\mathbf{a}_\mathrm{T}^{(m)}(0)\\ &\quad - \sqrt{2}\int_0^t C_{\eta\mathrm{T}}^{(m)}(t-t')\,\overline{\nabla\boldsymbol{v}}^{(m)}(t')\,\mathrm{d}t'. \end{aligned} \qquad (\mathrm{A\,2})$$

In most situations (excluding high-frequency processes such as hypersonic waves) the velocity gradient $\overline{\nabla\boldsymbol{v}}$ is considered to be time independent or, at worst, to vary slowly within the correlation time. A new variable $\tau = t - t'$ can then be introduced which permits $\overline{\nabla\boldsymbol{v}}$ to be removed from the τ-integration. For $t \gg \omega_\eta^{-1}$, ω_T^{-1}, $\omega_{\eta\mathrm{T}}^{-1}$, the upper limit in the τ-integration can be replaced by infinity. Then the solutions of the homogeneous equations vanish for $t \to \infty$ (i. e. the gas has essentially arrived at the stationary state) and Eqs. (A 1), (A 2) take the form

$$\mathbf{a}_\eta^{(m)}(t\to\infty) = -\left(\sqrt{2}\int_0^\infty C_\eta^{(m)}(\tau)\,\mathrm{d}\tau\right)\overline{\nabla\boldsymbol{v}}^{(m)}\,, \qquad (\mathrm{A\,3})$$

$$\mathbf{a}_\mathrm{T}^{(m)}(t\to\infty) = -\left(\sqrt{2}\int_0^\infty C_{\eta\mathrm{T}}^{(m)}(\tau)\,\mathrm{d}\tau\right)\overline{\nabla\boldsymbol{v}}^{(m)}\,. \qquad (\mathrm{A\,4})$$

From Eqs. (21), (A 3) and with $\overline{\mathbf{p}} = \sqrt{2}\,p_0\,\mathbf{a}_\eta$ (friction pressure tensor), Eq. (23) is immediately obtained. Similarly, from Eqs. (22), (A 4) and the relation between the irreducible part of the dielectric tensor, $\overline{\boldsymbol{\epsilon}}$, and the tensor polarization $\mathbf{a}_\mathrm{T}$ (cf. Ref. [7]), viz.

$$\overline{\boldsymbol{\epsilon}} = -2\,\pi\,n_0(\alpha_\parallel - \alpha_\perp)\,\sqrt{\frac{2}{15}}\,\langle J^2/(J^2 - \tfrac{3}{4})\rangle_0^{1/2}\,\mathbf{a}_\mathrm{T}\,, \qquad (\mathrm{A\,5})$$

the expression, Eq. (24), for $\beta^{(m)}$ follows in straightforward manner. Thus the time correlation functions which are solutions of the homogeneous differential equations determine also the solutions of the corresponding inhomogeneous equations and therefore the transport coefficients.

Acknowledgements

One of the authors (A. G. ST. PIERRE) wishes to thank the Institut für Theoretische Physik of the University Erlangen-Nürnberg for the hospitality extended to him, and the Alexander von Humboldt-Stiftung for financial support. We thank Prof. Dr. L. WALDMANN for useful comments.

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